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(71) Applicant *(for all designated States except US)*: ENSO-GUTZEIT OY [FI/FI]; Tutkimuskeskus, SF-55800 Imatra (FI).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)* : VAHERI, Marja [FI/FI]; Lystimäenkuja 1 A, SF-02210 Espoo (FI). SALAMA, Nina [FI/FI]; Servinmaijantie 12 A 8, SF-02150 Espoo (FI). RUOHONIEMI, Kimmo [FI/FI]; Harakantie 586 as. 8, SF-55800 Imatra (FI).

(74) Agent: OY HEINÄNEN AB; Patenttitoimisto, Annankatu 31-33 C, SF-00100 Helsinki (FI).

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Claim 1
* Enzyme mixture containing hydrolytic and oxidizing enzymes w/ redox below 200mV

(54) Title: METHOD FOR PULP PRODUCTION

(57) Abstract

The present invention relates to a mechanical pulp production from a fibrous material, such as whole logs, chips, shavings or pulp ground in a single or several stages. For the purpose of lowering the specific energy consumption, the method uses enzyme treatment of the fibrous material. The invention is implemented by treating the fibrous material with an enzyme mixture consisting of hydrolytic and oxidizing enzymes whose redox potential level is adjusted to a value below 200 mV.

See :

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Enzymes in energy consumption.

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METHOD FOR PULP PRODUCTION

The present invention relates to mechanical pulp production from a fibrous material.

Fibrous material, such as whole logs, chips, shavings or pulp ground in a single or several stages, is processed to mechanical pulp mostly by mechanical methods. Friction is availed in the production of mechanical pulp. There, energy is transferred to wood in a compression/decompression process, whereby the internal structure of wood is decomposed by frictional heat, therein allowing the separation of individual fibers from each other.

In prior-art methods mechanical pulp is produced as either groundwood or refined pulp; these methods bearing, however, the drawback of an extremely high specific energy consumption in refining, while in compensation a definite advantage is achieved by the high yield (approx. 95 %) available. In more advanced forms of refining, use is made of heat (in TMP, thermomechanical pulping) or, possibly also, of chemicals (in CTMP, chemical thermomechanical pulping). Further, recent research has found that specific energy requirements in wood refining and grinding can be lowered by allowing white rot fungi to act on either the chips or single-ground pulp. The method is hampered, however, by the length of the required attack time which may be several days, even weeks. Furthermore, the fungal process must be carried out in sterile conditions. These factors prevent wide-scale and cost-effective use of the method.

Similarly, known in the art is that lignin can be modified with the help of a lignin-modifying enzyme as described in the patent publication PCT/EP87/00635. The exemplifying embodiment of the above-mentioned PCT publication makes use of enzymes produced by the white rot fungus *Phanerochaete chrysosporium*. The *Phanerochaete chrysosporium* fungus produces a lignin peroxidase enzyme for the purpose of lignin modification. However, economical production of this enzyme on an industrial scale with the help of the *Phanerochaete chrysosporium* fungus is not possible today. For the modification of lignin, some other species of white rot fungi produce laccase, that is, phenol oxidase that can be produced easily and economically also in industrial scale.

Thus, prior art has been incapable of using enzymes, e.g., laccase, in order to lower the specific energy consumption of groundwood pulp. This problem can mainly attributed to insufficient knowledge of the reaction mechanism between the enzyme and lignin.

During the development of the method in accordance with the invention it was unexpectedly discovered that the redox potential is capable of controlling the reaction between the enzyme and lignin. Depending on the redox potential level, the enzyme modifies the lignin structure in the fibrous material either so as to ease the separation of the fibers during the mechanical grinding, or alternatively, in the opposite way so as to promote polymerization, thereby increasing the strength properties of the fibrous materials. The present invention differs from the above-mentioned PCT publication in that the exemplifying embodiment of the PCT publication does not disclose

the importance of the redox potential level as the controlling factor in the reaction mechanism between the enzyme and the lignin of the fibrous material for the purpose of reducing specific energy consumption in mechanical pulp refining. Thus, by virtue of the present invention, it becomes possible in an economical and simple manner to control the reaction mechanism between the enzyme and lignin toward a desired direction through the adjustment of the redox potential level.

Research into the reduction of groundwood specific energy consumption also produced another novel revelation. Therein, at an appropriate redox potential level for the enzyme function, the fibrous material was additionally enzyme-treated with a hydrolytic enzyme in a suitable ratio to the treatment an the oxidizing enzyme. The hydrolytic enzyme affects both the hemicellulose and/or cellulose. The invention aims to use an appropriate amount of hydrolytic enzyme so that it acts only on the superficial layer of hemicellulose and/or cellulose thus promoting the separation of fibers from each other during the mechanical refining of pulp.

It is therefore an object of the present invention to provide a method capable of lowering specific energy consumption in refining from the prior art level. The invention is characterized in that the fibrous material is treated with an enzyme mixture consisting of hydrolytic and oxidizing enzymes whose redox potential level is adjusted to a value below 200 mV. When the fibrous material is treated with lignin-attacking enzymes produced by, e.g., the white rot fungi and with cellulose and/or hemicellulose attacking enzymes produced by, e.g.,

the *Trichoderma reesei* or the *Aspergillus* species fungi, either alone or in combination with the presence of oxidizing/reducing, antioxidizing or salt chemicals, the savings of specific energy consumption are achieved even with short reaction times while raw material sterilization simultaneously can be avoided.

The enzyme treatment in accordance with the invention can be performed for, e.g., whole logs, chips, shavings or pulp ground in a single or several stages. The enzyme function presumes, however, an efficient contact with a maximally large fiber area.

The goal of the enzyme treatment is to modify the structure of the hemicellulose and/or cellulose in the fiber lignin so that the separation of the fibers becomes easier during the mechanical pulp refining. The desired result is achieved by treating the fibrous material with an oxidizing and a hydrolytic enzyme, and adjusting the redox potential with an appropriate oxidizing/reducing chemical. Advantageously, the enzyme used is laccase, hemicellulase, cellulase, pectinase, esterase or a mixture thereof. Appropriate enzymes deserving mentioning are xylanase, cellulase or pectinase enzymes produced by rot fungi or bacteria such as the *Trametes hirsutus* or *Trichoderma reesei* species. Temperature during the enzyme treatment can be within the range 10...90 °C, preferably within 40...70 °C while the pH is held within the range 2.0...10.0, preferably within 4.0...8.0 and the redox potential is held below 200 mV, preferably within -100...+100 mV.

In the following, the invention will be examined in more detail with the help of exemplifying embodiments based on laboratory tests.

Example 1.

2000 g (solids weight) of single-stage refined fir TMP was diluted in tap water so as to achieve 2.9 % pulp consistency. A laccase enzyme from *Polyporus hirsutus* was added to the mixture so that the laccase activity of the mixture became 0.5 U/ml while xylanase from *Trichoderma reesei* was added to the mixture so that the xylanase activity reached 5 U/grams of pulp. Temperature during the enzyme treatment was held at 20 °C, treatment time was 30 min, and the redox potential was held within the range -100...+100 mV. Prior to the enzyme addition, ascorbic acid (0.3 g/l) and NaCl were added to the mixture so that the NaCl concentration of the mixture became 10 mM.

After the enzyme treatment, sodium hydroxide (4 % of pulp solids weight) was added to the mixture. The mixture was manually agitated for 30 min. Finally, the mixture was thickened, centrifuged, homogenized and deep-frozen.

The pulp was next refined in a 30 cm dia. refiner by Sprout Waldro using a tapering disc clearance. The refining was performed twice and the specific energy consumption was measured. After each refining run, a sample of 200 g (solids weight) was taken. The samples were analyzed for freeness (CSF), fiber distribution, fiber length and shive content. In addition, the samples were processed into a white-water sheet which was measured for

density, tensile strength, tear index, light scatter coefficient, light absorption coefficient and brightness.

The refining result and the analysis values characterizing the pulp quality are given in Tables 1 and 2.

In addition to the above-described test (Test 1) exemplifying the invention, a reference test (Test 2) was performed whose results are correspondingly given in Table 1 below. The tests were carried out in the following conditions:

Test 2 (reference test): The pulp was not subjected to enzyme treatment but the pulp was simply treated with tap water in conditions similar to those prevailing during the enzyme treatment of Test 1. For the remaining parts, the treatment was analogous to that described above (Test 1).

As is evident from the results, it was possible to lower the specific energy consumption in refining by approx. 30 % when single-stage refined thermomechanical pulp (TMP) was subjected to enzyme treatment according to the invention simultaneously with lignin-modifying and hemicellulase/cellulase-type enzymes. In addition, the redox potential level in the enzyme mixture was monitored to stay below 200 mV during the reaction.

Furthermore, it can be noted that the brightness of the enzyme-treated pulps was better than that of the reference pulps.

For those versed in the art it is obvious that the invention is not limited by the exemplifying embodiments described above but it can be modified within the claims disclosed herein.

TABLE 1

REFERENCE PULP		ENZYME-TREATED PULP	
CSF (ml)	E (MJ/kg)	CSF (ml)	E (MJ/kg)
410		410	
	3.10		1.45
315		320	
	1.95		2.00
225		195	
	5.05		3.45

TABLE 2:

		TEST 1			TEST 2		
Pulp ID		0	I	II	0	I	II
Solids	%	33.17	30.05	29.08	35.56	31.59	29.09
CSF		~400	320	195		315	225
CENTRAL LAB.		45	46	47	14	15	16
Freeness	°FR	426	319	186	424	286	229
Shive content	%	4.48	1.60	0.28	3.05	2.67	(4.34)
Rejects	%	25.30	4.54	12.28	12.84	7.10	8.34
Bauer-McNett screening							
30-mesh fraction	%	49.8	46.4	40.1	53.8	49.4	45.5
50-mesh fraction	%	23.8	24.9	26.1	22.8	21.9	22.2
100-mesh fraction	%	7.4	7.4	7.9	7.5	6.7	6.9
200-mesh fraction	%	4.3	4.4	4.9	4.2	4.1	4.3
Fines	%	14.7	16.9	21.0	11.7	17.9	21.1
Fiber length analysis with Kajaani FS 200							
Average	mm	0.47	0.48	0.47	0.49	0.44	0.48
L-weighted	mm	1.30	1.32	1.28	1.35	1.27	1.34
W-weighted	mm	1.94	1.96	1.87	2.00	1.92	1.99
<0.20 mm p	%	47.67	46.64	46.49	46.67	48.97	47.52
<0.20 mm w	%	8.00	7.81	7.74	7.74	8.83	7.97
White-water sheet no.		45	46	47	14	15	16
Base weight	g/m^2	64.2	63.5	65.4	60.3	62.6	62.5
Thickness	µm	232	203	183	209	190	170
Density	kg/m^3	276	313	356	289	329	368
Tensile index	Nm/g	18.0	23.7	32.0	21.2	28.7	37.3
Elongation	%	1.4	1.4	1.7	1.6	1.8	1.9
Tear index	mNm^2/g	5.61	6.81	7.84	5.76	7.43	7.16
Light scat. coeff.	m^2/kg	39.3	44.1	44.3	38.2	40.6	42.8
Light abs. coeff.	kg/m^2	2.53	4.47	4.18	4.68	4.44	4.56
Brightness	%	47.2	49.7	50.0	45.6	47.1	47.6

WHAT IS CLAIMED IS:

1. A method for producing mechanical pulp from a fibrous material, c h a r a c t e r i z e d in that the fibrous product is treated with an enzyme mixture consisting of hydrolytic and oxidizing enzymes whose redox potential level is adjusted to a value below 200 mV.

2. A method as claimed in claim 1, c h a r a c t e r - i z e d in that the reaction mechanism between the enzyme and the lignin of the fibrous material is controlled by adjusting the redox potential level.

3. A method as claimed in claim 1 or 2, c h a r a c - t e r i z e d in that the redox potential level is adjusted in the range -100...+100 mV.

4. A method as claimed in any foregoing claim, c h a r - a c t e r i z e d in that the redox potential of the enzyme mixture is controlled by introducing appropriate oxidizing/reducing chemicals.

5. A method as claimed in any foregoing claim, c h a r - a c t e r i z e d in that the enzyme mixture used acts on the lignin, hemicellulose and/or cellulose of the fibrous material.

6. A method as claimed in any foregoing claim, c h a r - a c t e r i z e d in that the enzyme used is preferredly laccase, hemicellulase, cellulase, pectinase, esterase or a mixture thereof.

7. A method as claimed in any foregoing claim, c h a r a c t e r i z e d in that the enzyme treatment is carried out within the temperature range 10...90 °C, preferredly within 40...75 °C at a pH held within 2.0...10.0, preferredly within 4.0...8.0.

8. Use of enzymes acting on lignin, hemicellulose and/or cellulose of the fibrous material for the purpose of lowering specific energy consumption in mechanical pulp refining.

9. Use of an enzyme claimed in claim 8 for the purpose of reducing specific energy consumption in mechanical pulp refining when using oxidizing and hydrolytic enzymes.

10. Use of an enzyme claimed in claim 8 for the purpose of lowering specific energy consumption in mechanical pulp refining when using oxidizing/reducing chemicals.

11. Use, as claimed in any of claims 8...10, of laccase, hemicellulase, cellulase, pectinase, esterase or a mixture thereof for the purpose of lowering specific energy consumption in mechanical pulp refining.

INTERNATIONAL SEARCH REPORT

International Application No PCT/FI 91/00034

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC5: D 21 B 1/02, 1/16

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
IPC5	D 21 B; D 21 C

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in Fields Searched[8].

SE,DK,FI,NO classes as above

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category *	Citation of Document,[11] with indication, where appropriate, of the relevant passages[12]	Relevant to Claim No.[13]
Y	WO, A1, 8803190 (CALL, HANS-PETER) 5 May 1988, see page 2, line 21 - page 3, line 35 --	1-11
Y	Svensk Papperstidning No 8, 1980, L. Samuelsson et al, "Influence of fungal treatment on the strength versus energy relationship in mechanical pulping", page 221 - page 225 --	1-11
Y	SE, B, 412422 (DEFIBRATOR AB) 3 March 1980, see page 2, line 21 - page 3, line 34 --	1-11
A	EP, A1, 0060467 (EISENSTEIN, ALBIN ET AL) 22 September 1982, see the whole document --	

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IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
7th May 1991	1991 -05- 1 3
International Searching Authority	**Signature of Authorized Officer**
SWEDISH PATENT OFFICE	Marianne Bratsberg Marianne Bratsberg

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ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO.PCT/FI 91/00034

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the Swedish Patent Office EDP file on 91-03-23
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Patent document cited in search report	Publication date	Patent family member(s)		Publication date
WO-A1- 8803190	88-05-05	AU-B-	605215	91-01-10
		AU-D-	8230387	88-05-25
		DE-A-	3636208	88-05-05
		EP-A-	0327576	89-08-16
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